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Report No.

QL0235/0113

~~Aerojet-General~~ CORPORATION

AZUSA, CALIFORNIA

INFORMAL REPORT OF PROGRESS

Copy No. 3

8 January 1962

TO: Director
Advanced Research Projects Agency
The Pentagon
Washington 25, D.C.

VIA: Chief
Office of Naval Research
Department of the Navy
Washington 25, D.C.

Attn: Propulsion Chemistry Branch, Code 426

~~ARPA Order Number: 170-61~~
~~Project Code Number: 9100~~
~~Contractor: Aerojet-General Corporation, Azusa, Calif.~~
~~Contract Number: Nonr 2655(00)~~
~~Date of Contract: 1 September 1958~~
~~Amount of Contract: \$549,371.00~~
~~Contract Expiration Date: 31 August 1962~~
Project Engineer: N. W. Thomas
EDgewood 4-6211, Extension 6107
Title: Research in Fluoro-Nitro Compounds (U)
(Unclassified Title)
Period Covered: 1 October 1961 through 31 December 1961

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This is the third in a series of quarterly letter reports submitted in partial fulfillment of the contract.

AEROJET-GENERAL CORPORATION

J. R. Funder
D. L. Armstrong
Director of Chemistry

United States Patent Office Secrecy Order

NOTICE

The Aerojet-General Corporation has filed patent applications in the U.S. Patent Office to cover inventions disclosed in this publication, and the Commissioner of Patents has issued a secrecy order thereon.

Compliance with the provisions of this secrecy order requires that those who receive a disclosure of the secret subject matter be informed of the existence of the secrecy order and of the penalties for the violation thereof.

The recipient of this report is accordingly advised that this publication includes information which is now under a secrecy order. It is requested that he notify all persons who will have access to this material of the secrecy order.

Each secrecy order provides that any person who has received a disclosure of the subject matter covered by the secrecy order is

"in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any person not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents."

Although the original secrecy order forbids disclosure of the material to persons not cognizant of the invention prior to the date of the order, a supplemental permit attached to each order does permit such disclosure to:

- "(a) Any officer or employee of any department, independent agency, or bureau of the Government of the United States.
- "(b) Any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the disclosure of the above indicated application for use in the prosecution of the war.

"The principals under the secrecy are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of the secrecy order."

No other disclosures are authorized, without written permission from the Commissioner of Patents. Public Law No. 239, 77th Congress, provides that whoever shall "willfully publish or disclose or authorize or cause to be published or disclosed such invention, or any material information with respect thereto," which is under a secrecy order, "shall, upon conviction, be fined not more than \$10,000 or imprisoned for not more than two years or both." In addition, Public Law No. 700, 76th Congress, provides that the invention in a patent may be held abandoned, if it be established that there has been a disclosure in violation of the secrecy order.

It must be understood that the requirements of the secrecy order of the Commissioner of Patents are in addition to the usual security regulations which are in force with respect to activities of the Aerojet-General Corporation. The usual security regulations must still be observed notwithstanding anything set forth in the secrecy order of the Commissioner of Patents.

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Report No. Q10235-C1-3

I. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE

The reaction of methylallylacetone with difluoramine in sulfuric acid gave 2,5,5-trimethyl-2-(difluoramino)tetrahydrofuran, identical to the product previously prepared from 5-methyl-5-nitro-2-hexanone.

Some additional examples of the Michael addition of difluoramine were examined. Whereas it had previously been observed that methyl acrylate gave methyl β -difluoramino-propionate, methyl methacrylate did not react. Styrene, acrylamide and 3-methyl-1-butene-3-yne decomposed under the reaction conditions.

The expected gem-difluoramines were prepared from 3-methyl-2-pentanone, n-heptaldehyde and 2,7-octanedione.

The reaction of ethoxyacetylene with difluoramine gave a mixture of NF compounds apparently including $\text{CH}_2=\text{C}(\text{NF}_2)\text{OC}_2\text{H}_5$ and $\text{FCH}_2-\text{C}=\text{NF}(\text{OC}_2\text{H}_5)$. The addition of difluoramine to dicyclohexylcarbodiimide appears to have given a monoadduct. The reaction of cyclobutanone with difluoramine in sulfuric acid gave a product which analyzed as a fluorimino compound. Several new NF compounds were formed from the reaction of t-butyl hydroperoxide with difluoramine. Work is being continued to identify the products of these reactions.

B. FLUORINATION STUDIES

The aqueous fluorination of diethyl methylenedicarbamate gave a trace of bis(difluoramino)methane as well as diethyl N,N'-difluoromethylenedicarbamate, ethyl difluoraminoethylcarbamate (or its isomer, ethyl N,N'-difluoraminoethylcarbamate) and ethyl N-difluoraminoethyl-N-fluorocarbamate.

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Report No. Q10235-01-3

The fluorination of diethyl ethylenedicarbamate gave diethyl N,N'-difluoroethylenedicarbamate, and ethyl β -difluoraminoethylfluorocarbamate, as well as a trace of 1,2-bis(difluoramino)ethane.

The fluorination of methylenediacetamide and methylenediformamide gave low yields of bis(difluoramino)methane.

The fluorination of allylurea resulted in a C-N bond cleavage, with the formation of N,N-difluorourea. The fluorination of cyanoguanidine also gave some N,N-difluorourea.

The material having a low boiling point found in the fluorination of arylureas was shown to be trichlorofluoromethane.

II RECOMMENDATIONS AND FUTURE PLANS

A. REACTIONS OF DIFLUORAMINE

The immediate emphasis in this area will be placed on the identification of the product obtained from ethoxyacetylene, *t*-butyl hydroperoxide, and dicyclohexylcarbodiimide. These investigations might ultimately give compounds with three NF_2 groups on a carbon, $-\text{ONF}_2$ compounds, and tetrakis(difluoramino)-methane respectively. The investigation of the effect of structural features on the reactions of carbonyl and acetylenic compounds with difluoramine will also be continued.

B. FLUORINATION STUDIES

The study of the fluorination of polyfunctional ureas and carbamates will be continued with the objective of preparing compounds with high N-F content. In addition, the reactions of N-fluorocarbamates will be studied. Thus, the acidic NH of N-fluorocarbamates might react with carbonyl compounds in a reaction similar to that of HNF_2 . The hydrolysis of N-fluorocarbamates could yield fluoramine or the alkyl derivatives. The former could be used for the preparation of fluorimines from carbonyl compounds.

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